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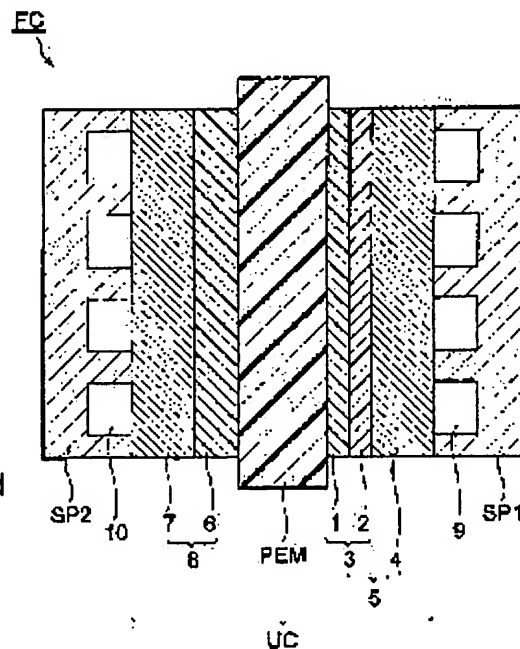
(54) SOLID POLYMER FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a solid polymer fuel cell in which occurrence of flooding is sufficiently prevented even in flowing a large current at the starting stage of driving and a high battery output can be obtained stably from the starting stage for a long period.

SOLUTION: The fuel cell FC comprises an anode 8, a cathode 5 and a polymer electrolyte membrane PEM arranged between the anode and the cathode, and the cathode comprises a gas dispersing layer 4 and a catalyst layer 1 and a catalyst layer 2 which are arranged between the gas dispersing layer and the polymer electrolyte membrane. The percentage of water content W1 (%) of the ion exchange resin contained in the catalyst layer 1 adjoining the polymer electrolyte

membrane and the percentage of water content W2 (%) of the ion exchange resin contained in the catalyst layer 2 adjoining the gas dispersion layer satisfy respectively the following conditions at the same time; $10 \leq W1 < 100 \dots (1)$, $5 \leq W2 < 80 \dots (2)$, $5 \leq (W1 - W2) \leq 45 \dots (3)$.



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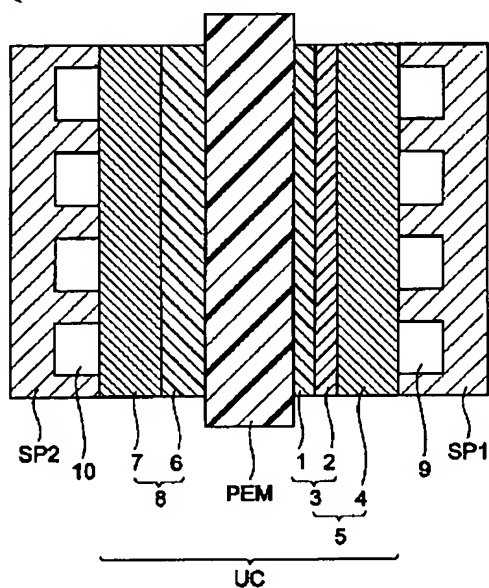
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DRAWINGS

[Drawing 1]

FC



[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a polymer electrolyte fuel cell.

[0002]

[Description of the Prior Art] The product by the cell reaction is water theoretically, and the fuel cell attracts attention as a clean generation-of-electrical-energy system which does not almost have a bad influence to earth environment.

[0003] especially the polymer electrolyte fuel cell that has the polyelectrolyte film -- (1) -- the cell property improved by leaps and bounds by using the catalyst support carbon particle covered with that the polyelectrolyte film which has high ion conductivity was developed, (2) polyelectrolyte film, congener, or ion-exchange resin (polyelectrolyte) of a different kind as a component of an electrode catalyst bed, and having come to attain three-dimension-ization of the reaction site in the so-called catalyst bed etc. And in addition to the ability to acquire such a high cell property, since the formation of small lightweight is easy, as for the polymer electrolyte fuel cell, the utilization as migration cars, such as an electric vehicle, a power source of a small cogeneration system, etc. is expected.

[0004] And the polymer electrolyte fuel cell by which current examination is carried out Since the operating temperature field is generally as low as 50-120 degrees C and cannot use the exhaust heat easily due to constraint of heat-resistant [of the polyelectrolyte film], ion conductivity, etc. The engine performance which can obtain high generating efficiency and high power density especially under the high actuation condition of rates of cathode reaction gas utilization, such as rates of anode reaction gas utilization, such as pure hydrogen, and air, is demanded towards the utilization.

[0005] Usually, the gas diffusion electrode used for a polymer electrolyte fuel cell consists of a catalyst bed containing the catalyst support carbon particle covered with the above-mentioned ion-exchange resin, and a gaseous diffusion layer which collects the charge generated in a catalyst bed while supplying reactant gas to this catalyst bed. And in the catalyst bed of a gas diffusion electrode, the opening section which consists of very small pore formed between the aggregated particles of the carbon particle used as the above-mentioned component or between the Miyoshi particles exists, and the opening section concerned is functioning as diffusion passage of reactant gas.

[0006] However, under the actuation conditions that the reaction rate of the above cell reactions is comparatively high, the amount of the water (henceforth proton company water) which moves in connection with the proton which moves towards a cathode in the inside of the polyelectrolyte film from an anode, and the amount of the generation water which generates according to the electrode reaction of a cathode and is condensed increase. Therefore, these water is not promptly discharged outside from a cathode, but the phenomenon in which the opening section in the catalyst bed of a cathode will be blockaded with these water, and the phenomenon of the so-called flooding tended to happen. When such flooding happens, supply to the reaction site of the catalyst bed of cathode reaction gas is barred, and it becomes impossible to obtain a desired cell output stably. Therefore, generating of flooding is prevented, and in order to be stabilized and to obtain a desired cell output over a long period of time, reservation of the good wastewater nature of a cathode is needed.

[0007] Therefore, the polymer electrolyte fuel cell which made fluorine-containing resin, such as polytetrafluoroethylene (henceforth PTFE), tetrafluoroethylene / hexafluoropropylene copolymer, and tetrafluoroethylene / perfluoro (alkyl vinyl ether) copolymer, etc. contain in a cathode catalyst bed is proposed by JP,5-36418,A as a water repellent agent. However, although the water-repellent high opening section could be built by the water repellent agent when the water repellent agent was made to

contain in a catalyst bed in this way, there was a problem that a cell output may decline on the contrary, by the fall of the gaseous diffusion nature in the catalyst bed by increase of the electric resistance of the electrode by the insulation of a water repellent agent, and increase of the thickness of a catalyst bed. In addition, a "A/B copolymer" shows [be / it / under / this / specification / setting] the copolymer which consists of a polymerization unit based on A, and a polymerization unit based on B.

[0008] Moreover, a catalyst bed is prepared, respectively, the catalyst bed containing the high ion-exchange resin of IEC is arranged to a polyelectrolyte film side, using as a component two kinds of catalyst support carbon particles covered with the ion-exchange resin with which ion exchange capacity (henceforth IEC) differs to JP,11-288727,A, and the polymer electrolyte fuel cell which has the cathode catalyst bed of the two-layer structure which has arranged the catalyst bed containing the low ion-exchange resin of IEC to the gaseous diffusion layer side is proposed.

[0009]

[Problem(s) to be Solved by the Invention] However, even if this invention persons are polymer electrolyte fuel cells given in above-mentioned JP,11-288727,A If the cell output in early stages of starting tends to be made high and it is going to pass a high current, a cell output will decline comparatively from starting for a short time. furthermore, the problem that the flooding in a cathode catalyst bed will occur -- or If it is going to prevent the flooding in a cathode catalyst bed, the cell output in early stages of starting will become low, therefore there is a problem of it becoming impossible to continue a high cell output for a long period of time, and it found out that it was not yet enough.

[0010] It is made in view of the technical problem which the above-mentioned conventional technique has, even if it is the case where a high current is passed in the early stages of starting, generating of flooding is fully prevented, and this invention aims at offering the polymer electrolyte fuel cell which is stabilized and can obtain a high cell output from the early stages of starting over a long period of time.

[0011]

[Means for Solving the Problem] As a result of repeating research wholeheartedly so that this invention persons may attain the above-mentioned purpose, the cause of the problem which the polymer electrolyte fuel cell of a publication has in this JP,11-288727,A When the water content W1 of the ion exchange resin contained in the catalyst bed arranged at a polyelectrolyte film side and the water content W2 of the ion exchange resin contained in the catalyst bed arranged at a gaseous diffusion layer side are computed, These differences (W1-W2) found out that it was in about 3 - 4%, and a small thing.

[0012] This invention is a polymer electrolyte fuel cell which has the polyelectrolyte film arranged between an anode, a cathode, and an anode and a cathode. A cathode Then, a gaseous diffusion layer, Two or more catalyst beds arranged between gaseous diffusion layers and polyelectrolyte film concerned, Preparation ***** , the water content W1 of the ion exchange resin contained in the catalyst bed of the innermost section which touches the polyelectrolyte film [%], And the water content W2 of the ion exchange resin contained in the catalyst bed of the outermost part which touches a gaseous diffusion layer [%] is condition: $10 \leq W1 < 100$ of following type (1) - (3). -- (1), $5 \leq W2 < 80$ -- (2) $5 \leq (W1-W2) \leq 45$ -- The polymer electrolyte fuel cell characterized by filling (3) to coincidence is offered.

[0013] Here, in this specification, "the water content W of ion exchange resin" is a value based on following type (4): $W = \{(X_w - X_d) / X_d\} \times 100$ --(4). In addition, X_w shows the swelling mass measured after holding ion exchange resin in 90-degree C warm water, and returning to a room temperature underwater further among a formula (4), and X_d shows the dry mass measured after returning to a room temperature by nitrogen-gas-atmosphere mind further, after carrying out reduced pressure drying of the ion exchange resin. And W1 shows the water content of the ion exchange resin contained in the catalyst bed of the innermost section, and W2 shows the water content of the ion exchange resin contained in the outermost catalyst bed.

[0014] Thus, each can be clearly differentiated to the catalyst bed of the innermost section, and the function which mainly bears the wastewater to the exterior of produced water or proton company water for the function which mainly bears electrode reaction to the outermost catalyst bed can be given to it because the value of above W1 and W2 makes the value of (W1-W2) 5% or more within limits which fulfill the conditions of (1) and (2).

[0015] Namely, although moisture content in the catalyst bed concerned cannot become low and a reaction site cannot be effectively used the way things stand since the catalyst bed of the innermost section which touches the polyelectrolyte film has few amounts of accumulation of produced water It can be made to be able to hold in the condition of having made high enough moisture content in the catalyst bed concerned, many reaction sites can be secured, and electrode reaction can be made to

perform efficiently in this invention by distributing the ion exchange resin which has the high water content W intentionally in the catalyst bed of the innermost section. On the other hand, although the moisture content in the catalyst bed concerned becomes high and possibility that flooding will occur becomes high at this rate since the catalyst bed of the outermost part which touches a gaseous diffusion layer has many amounts of accumulation of produced water. By distributing the ion exchange resin which has the low water content W intentionally in the outermost catalyst bed in this invention, it can be made to be able to hold in the condition of having made low enough moisture content in the catalyst bed concerned, water-repelling nature in the catalyst bed concerned can be made high, the outstanding wastewater nature can be given, and the wastewater to the exterior of produced water or proton company water can be made to perform efficiently.

[0016] Consequently, in the catalyst bed field near the polyelectrolyte film, since many reaction sites are used effectively, high-power-density-ization of a cell can be attained, and on the other hand, in the catalyst bed field near the gaseous diffusion layer, since produced water and proton company water can be drained outside smoothly, prevention of generating of flooding can be aimed at. Therefore, in the electrode of the polymer electrolyte fuel cell under actuation, the catalyst bed which can hold sufficient supply of the reactant gas to a reaction site and a proton over a long period of time and which has good wastewater structure can be built by constituting a polymer electrolyte fuel cell in this way, preventing generating of flooding.

[0017] If the value of the difference (W1-W2) of the water content W1 of the ion exchange resin contained in the catalyst bed of the innermost section and the water content W2 of the ion exchange resin contained in the outermost catalyst bed is less than 5% here it becomes difficult to differentiate clearly the function of the catalyst bed of the innermost section and the outermost catalyst bed which is alike, respectively, receives and mainly bears electrode reaction to the former, and the function which mainly bears the wastewater to the exterior of produced water or proton company water to the latter, and to give it. On the other hand -- this (W1-W2) -- when a value exceeds 45%, the movement magnitude of the water from ion exchange resin to the ion exchange resin in the catalyst bed by the side of a gaseous diffusion layer in the catalyst bed by the side of the polyelectrolyte film becomes large, and it becomes impossible for the ion exchange resin in the catalyst bed by the side of a gaseous diffusion layer to be unable to discharge water moreover -- this (W1-W2) -- as for a value, it is more desirable from the same viewpoint as the above that it is 5 - 20%.

[0018] If the water content W of ion exchange resin becomes less than 5%, it will become difficult to acquire sufficient proton conductivity and a cell output will decline. On the other hand, if the value of this W becomes 100% or more, the wastewater nature in a catalyst bed will become it is remarkable and inadequate, and flooding will occur.

[0019] For this reason, in order to make it above W1 and W2 go into less than 100% of range 5% or more, about less than [of (1) type / more than condition: 10%100%], and W2, it may be [in / both / this invention / 1 / W] less than [of (2) types / more than condition: 5%80%]. Moreover, as for this W1, it is more desirable that it is 15 - 60% from a viewpoint which gave [above-mentioned] explanation, and, as for W2, on the other hand, it is more desirable that it is 10 - 50%.

[0020]

[Embodiment of the Invention] Hereafter, the suitable operation gestalt of the polymer electrolyte fuel cell of this invention is explained to a detail, referring to a drawing.

[0021] Drawing 1 is the sectional view showing the unit cell and separator concerning the suitable operation gestalt of the polymer electrolyte fuel cell of this invention. This fuel cell FC consists of a plate-like unit cell UC and two separators SP1 and SP2 arranged at the both sides of a unit cell UC. These separators SP1 and SP2 are for forming with the cathode reaction gas passageway 9 and the anode reaction gas passageway 10, respectively. Furthermore, the unit cell UC consists of a cathode 5, an anode 8, and polyelectrolyte film PEM that has proton conductivity.

[0022] The hydrogen content gas (fuel gas) generated by carrying out steam reforming of a methanol or a hydrocarbon system Hara fuel called natural gas as an electrode active material of this fuel cell FC, for example is used as anode reaction gas, for example, oxygen content gas, such as air, is used as cathode reaction gas. And in an anode 8, in a cathode 5, the electrode reaction shown, respectively advances at following (5) ceremony, all the cell reactions shown in (7) types as a whole advance at it, and electrical energy occurs at it at the following (6) types.

$H_2 \rightarrow 2H^{++} + 2e^-$ -- (5)

$(1/2) O_2 + 2H^{++} + 2e^- \rightarrow H_2O$ -- (6)

$H_2 + (1/2) O_2 \rightarrow H_2O$ -- (7)

[0023] Hereafter, based on drawing 1, the detail of each component of this operation gestalt is explained. The polyelectrolyte film PEM is formed of solid-state polymeric materials, such as a fluorine polymer, and is ion exchange membrane which shows good ion conductivity under a damp or wet condition. The perfluorocarbon polymer which has the perfluorocarbon polymer (henceforth a sulfonic acid type perfluorocarbon polymer) which has a sulfonic group, polysulphone resin, a phosphonic acid radical, or a carboxylic-acid radical as solid-state polymeric materials which constitute the polyelectrolyte film PEM can be used. Especially, a sulfonic acid type perfluorocarbon polymer is desirable, and Nafion (Du Pont make), the deflection myon (Asahi Glass Co., Ltd. make), etc. are mentioned as goods.

[0024] On the other hand, the cathode 5 and anode 8 which are a gas diffusion electrode all consist of the gaseous diffusion layer 4 and a gaseous diffusion layer 7, and the catalyst bed 3 and catalyst bed 6 that were formed on these gaseous diffusion layers.

[0025] About the fuel gas or air supplied to the single cell UC, the gaseous diffusion layer 4 and the gaseous diffusion layer 7 are smooth to a catalyst bed side, and a thing which bears the role which emits outside the role and produced water which make the charge produced according to the electrode reaction shown in the above (5) and (6) types in a catalyst bed 3 and a catalyst bed 6 emit to the exterior of the single cell UC, a unconverted gas, etc. while supplying homogeneity. As a component of the gaseous diffusion layer 4 and the gaseous diffusion layer 7, the porous body (for example, the carbon cross and carbon paper with which the layer which consists of a water repellent agent and carbon powder was formed in the front face) which has electronic conduction nature is used, for example.

[0026] The cathode catalyst bed 3 of a fuel cell FC serves as a reaction place where the electrode reaction shown in the above-mentioned (6) formula occurs. The cathode catalyst bed 3 is constituted considering the catalyst support carbon black particle with the big surface area which covered ion-exchange resin as a subject.

[0027] As shown in drawing 1, this catalyst bed 3 consists of a catalyst bed 1 arranged at the polyelectrolyte film PEM side, and a catalyst bed 2 arranged at the gaseous diffusion layer 4 side. Water content W1% of the ion exchange resin which contains these catalyst beds 1 and catalyst beds 2 in the catalyst bed 1 which touches the polyelectrolyte film PEM And water content W2% of the ion exchange resin contained in the catalyst bed 2 which touches a gaseous diffusion layer is condition: $10 \leq W1 < 100$ of following formula (1) - (3), respectively. -- (1) $5 \leq W2 < 80$ -- (2) $5 \leq (W1 - W2) \leq 45$ -- It is formed as (3) is filled to coincidence.

[0028] as state previously, when fulfill the conditions of this (1) - (3) type to coincidence, the ionic conduction path and the gaseous diffusion path which it be influence of the generation water of a cell reaction and proton company water among the supply ways to the ion in a catalyst bed 3, reactant gas, and an electronic reaction site can be secure with sufficient balance during actuation of a fuel cell FC.

[0029] That is, in a catalyst bed 1, since the water content W of the contained ion exchange resin is high, the path which a proton can fully move can be secured and a reaction site can be prepared widely. In addition, although the produced water accumulated while moving towards the thickness direction of a catalyst bed 1 in a catalyst bed 1 from the interface of a condensed part, and the polyelectrolyte film PEM and catalyst bed 1 of the proton company water which moves in the inside of the polyelectrolyte film PEM exists The amount of water which doubled these is little as compared with the amount of water in a catalyst bed 2 as there are few accumulated parts of produced water, and water content W does not cause big trouble to gaseous diffusion nature as it is high. And as for the burden of wastewater, for a certain reason, the back-diffusion-of-electrons water which makes driving force the concentration gradient of the water from a cathode 3 to an anode 8 near the polyelectrolyte film PEM will also be mitigated further. Since the water content W of the contained ion exchange resin is low in a catalyst bed 2, it becomes easy to repel water and wastewater nature becomes good, although very a lot of [the part of accumulation generation water] water exists on the other hand as compared with a catalyst bed 1, while discharging a lot of water outside efficiently, the path which gas diffuses is fully securable.

[0030] Thus, in the catalyst bed 3, the good wastewater structure where supply of smooth reactant gas to the secured reaction site can be held over a long period of time is built. Therefore, since it becomes possible to prevent generating of the flooding in the catalyst bed 3 under actuation, and to use effectively the reaction site in the catalyst bed 3 concerned, over a long period of time, it is stabilized and a high cell output can be obtained from the early stages of starting.

[0031] Moreover, as for the ion-exchange resin contained in a catalyst bed 1 and a catalyst bed 2, it is desirable that it is a sulfonic acid type perfluorocarbon polymer. A sulfonic acid type perfluorocarbon polymer enables stable and prompt proton conduction chemically in a catalyst bed 1 and a catalyst bed 2

for a long period of time.

[0032] Such a sulfonic acid type perfluorocarbon polymer has the desirable copolymer which consists of a polymerization unit (the integer of 1-12 and p of the integer of 0-3 and n is [m] 0 or 1 among a formula, and Z is F or CF₃) based on the fluoro vinyl compound expressed in CF₂=CF-(OCF₂CFZ) m-Op-(CF₂) n-SO₃H as the polymerization unit based on tetrafluoroethylene.

[0033] As a desirable example of the above-mentioned fluoro vinyl compound, the compound of (i) - (iv) is mentioned below. However, among the following type, in the integer of 1-8, and r, the integer of 1-8 and s show the integer of 1-8, and t shows [q] the integer of 1-3.

CF₂=CFO(CF₂)_qSO₃H (i)

CF₂=CFOCF₂CF(CF₃)O(CF₂)_rSO₃H (ii)

CF₂=CF(CF₂)_sSO₃H (iii)

CF₂=CF(OCF₂CF(CF₃))_tO(CF₂)₂SO₃H (iv)

[0034] In addition, as long as the polymerization unit based on a fluorine-containing olefin or perfluoro (alkyl vinyl ether), such as hexafluoropropylene, is below 25 mass % of the polymerization unit based on tetrafluoroethylene, it replaces the polymerization unit based on tetrafluoroethylene, and may be included in the above-mentioned copolymer.

[0035] Furthermore, as an approach of controlling on the conditions of (1) - (3) type of having stated previously the water content W of the ion exchange resin contained, respectively to the catalyst bed 1 and the catalyst bed 2, there are an approach of controlling by IEC of ion exchange resin, the approach of controlling by molecular weight of ion exchange resin, etc. For example, when controlling the water content W of ion exchange resin by IEC of ion exchange resin, it can carry out easily by changing the synthetic conditions of ion exchange resin, such as polymerization conditions of a monomer used as a raw material. Moreover, when controlling the water content W of ion exchange resin by molecular weight of ion exchange resin, it can carry out easily by changing the melting extrusion temperature of the precursor of the ion exchange resin which the synthetic conditions of ion exchange resin are changed and is obtained in a synthetic process etc.

[0036] In addition, IEC of ion exchange resin is a value [milliequivalent / g desiccation resin] (hereafter referred to as meq./g) defined by the number of equivalent of the ion exchange group contained in per 1g of desiccation resin, and the water content W of the ion exchange resin tends to become high, so that IEC of ion exchange resin is high. Moreover, the melting extrusion temperature (hereafter referred to as TQ) of a precursor is a numeric value used as the standard of the molecular weight of resin, and molecular weight becomes small, so that TQ is generally low. And since a debt of the chain in a crystallized state becomes easy to swell the ion exchange resin obtained few so that molecular weight is small, it will have the high water content W.

[0037] Moreover, about the content of the ion exchange resin contained in a catalyst bed 1 and a catalyst bed 2, respectively, also in any of a catalyst bed 1 and a catalyst bed 2, it is desirable that the range of the ratio (mass ratio) of a catalyst and ion exchange resin is mass =0.40:0.60-0.95:0.05 [of a catalyst] of mass:ion exchange resin, and it is more desirable that it is mass =0.60:0.40-0.80:0.20 [of a catalyst] of mass:ion exchange resin.

[0038] If the content of the catalyst over ion exchange resin is lower than the ratio [of a catalyst] of mass:ion exchange resin of mass =0.40:0.60 here, since the amounts of catalysts run short, there is an inclination for a reaction site to decrease. Moreover, there is an inclination for the thickness of the enveloping layer of the ion exchange resin which covers a catalyst to become large, and for the diffusion rate of the reactant gas in resin to become small. Furthermore, pore required for diffusion of reactant gas will be closed by resin, and there is a possibility of becoming easy to produce flooding. On the other hand, when the content of the catalyst over ion exchange resin exceeds the ratio [of a catalyst] of mass:ion exchange resin of mass =0.95:0.05, there is an inclination for the amount of the ion exchange resin which covers the catalyst concerned to a catalyst to be insufficient, for a reaction site to decrease, and for a cell output to decline. Moreover, although ion-exchange resin functions also as the binder of a cathode 5, and adhesives of a cathode 5 and the polyelectrolyte film PEM, the inclination for the functioning to become inadequate and for it to become impossible to maintain catalyst bed structure to stability becomes large. In addition, in the case of the support catalyst supported by support, such as catalyst support carbon, a catalyst here shall also contain the mass of the support.

[0039] Furthermore, in this invention, when pore volume with a pole diameter [to the total pore volume in the catalyst bed of each electrode] of 0.1 micrometers or less pays its attention comparatively (henceforth a "micropore rate"), as for the micropore rate of a catalyst bed 2, it is desirable that it is smaller than the micropore rate of a catalyst bed 1, and it is more desirable that the difference of the

micropore rate of a catalyst bed 2 and the micropore rate of a catalyst bed 1 is 5-80vol.%. In addition, in the following explanation, the opening section excellent in the gaseous diffusion nature which consisted of pores to which a pore diameter exceeds 0.1 micrometers, and wastewater nature is called "gaseous diffusion effective opening section" to a "micropore rate."

[0040] Thus, by controlling the pore diameter of the pore currently formed in each of a catalyst bed 1 and a catalyst bed 2 in addition to paying one's attention to the water content W of the ion exchange resin which each of a catalyst bed 1 and a catalyst bed 2 is made to contain Since the consistency of a reaction site can be made high in a catalyst bed 1 and wastewater nature can be made high in a catalyst bed 2, supply of smooth reactant gas to the reaction site in each catalyst bed It becomes possible to build more certainly the catalyst bed which has the good wastewater structure which can be held over a long period of time.

[0041] Especially, the function in which a catalyst bed 1 and a catalyst bed 2 have, respectively can be more clearly differentiated as mentioned above by carrying out the difference of the micropore rate in a catalyst bed 1, and the micropore rate in a catalyst bed 2 to more than 5vol(s).%. There is an inclination it to become difficult gradually to differentiate clearly the function which the catalyst bed 1 which said previously that the difference of the micropore rate in a catalyst bed 1 and the micropore rate in a catalyst bed 2 becomes under 5vol(s).%, and a catalyst bed 2 have, respectively. On the other hand, if the difference of the micropore rate in a catalyst bed 1 and the micropore rate in a catalyst bed 2 exceeds 80vol(s).%, the inclination it to become difficult gradually to maintain the structure of a catalyst bed will become large. Moreover, the inclination flooding becomes easy to generate in a catalyst bed 1 also becomes large.

[0042] Moreover, there is an inclination for the surface area in the pore in each catalyst bed to decrease remarkably if a micropore rate becomes under 10vol(s).%, for the area which reactant gas can contact to become small, and for a cell output to decline about each of the catalyst bed 1 of the cathode of this invention and a catalyst bed 2. On the other hand, if a micropore rate exceeds 98vol(s).%, the rate of the gaseous diffusion path in each catalyst bed decreases, and when operating a fuel cell FC under the conditions which a lot of water generates like a high current density field, the inclination which flooding generates will become large.

[0043] For this reason, in order to make it the micropore rate of the catalyst bed 1 of a cathode and a catalyst bed 2 go into the range of 10 - 98vol.%, as for the micropore rate in a catalyst bed 1, it is desirable that it is 40-98vol.%, and it is [in / both / this invention] more desirable that it is 60-96vol.%. on the other hand, the micropore rate in a catalyst bed 2 is also 10-93vol.% from the above-mentioned viewpoint -- good -- better -- it is desirable and it is more desirable that it is 40-90vol.%.

[0044] Thus, what is necessary is just to change the class of solvent of the liquid (henceforth catalyst bed formation ink) which dissolved or distributed ion exchange resin and a catalyst to the solvent at least, for example as an approach of controlling the pore structure of the opening section formed in each catalyst bed. For example, the direction which uses organic solvents, such as ethanol, toluene, and dichloropentafluoropropane, is more nearly able to acquire porous catalyst bed structure more than water.

[0045] Moreover, an ostomy agent and a foaming agent may be used as the other approaches. As an ostomy agent, a meltable calcium carbonate etc. is applicable to camphor (it has sublimability) or an acid, for example. That to which it is foamed a little as a foaming agent and efficiently is desirable, for example, there is inorganic system matter represented by the organic system matter represented by an azo compound, a nitroso compound, and the sulfonylhydrazide compound and a metal carbonate, a bicarbonate, a nitrite, and the hydride. Heat-treatment is made to decompose a foaming agent, and in order to generate gas, it is necessary to perform heat-treatment held at the temperature of 200-280 degrees C for 10 seconds to 30 minutes. In addition, in this heat-treatment, since the resin for catalyst covering may decompose, the shorter one of the processing time is desirable.

[0046] Moreover, as for the thickness of the cathode catalyst bed 3, it is desirable that it is 1-50 micrometers, and it is more desirable that it is 5-40 micrometers. While it is too thin in the thickness of the cathode catalyst bed 3 being less than 1 micrometer and formation of two or more layer structure of a bilayer is substantially difficult, it is in the inclination which stops easily being able to form the catalyst bed which has sufficient reaction site. On the other hand, if the thickness of the cathode catalyst bed 3 exceeds 50 micrometers, while the thickness of the catalyst bed 3 whole will become large and the gaseous diffusion nature of a catalyst bed 3 will fall remarkably, it is in the inclination for the ohmic resistance (electrical-potential-difference loss) of the catalyst bed 3 whole to increase. And as for each thickness of a catalyst bed 1 and a catalyst bed 2, it is desirable that it is 0.5-40 micrometers.

[0047] On the other hand, the catalyst bed 6 of the anode 8 of a fuel cell FC is also constituted by the catalyst support carbon black particle with the big surface area which covered ion-exchange resin. The catalyst bed 6 of an anode 8 bears the role which advances electrode reaction shown in the above-mentioned (5) formula.

[0048] As for the ion-exchange resin contained in the catalyst bed 6 of an anode 8, it is desirable that it is a sulfonic acid type perfluorocarbon polymer like a cathode 5. Moreover, since produced water does not arise in an anode 8, about five-cathode wastewater nature is unnecessary. In order to secure sufficient reaction site, a high thing has [the ion exchange resin in an anode 8] water content W desirable [therefore,].

[0049] As for IEC of the ion exchange resin contained in a catalyst bed 6 from the above viewpoints, it is desirable that it is 0.3-1.5meq./g. It becomes difficult for IEC of the ion exchange resin contained in a catalyst bed 6 to build proton conduction path sufficient in a catalyst bed 6 as it is under 0.3meq./g, and sufficient reaction site cannot be secured. On the other hand, if IEC of the ion exchange resin contained in a catalyst bed 6 exceeds 1.5meq./g, the wastewater nature in a catalyst bed 6 will fall, and the inclination which flooding generates in the catalyst bed 6 by condensation of humidification water will become large. Moreover, at drawing 1, although a catalyst bed 6 consists of a monolayer, it may consist of two or more layers.

[0050] In addition, a catalyst bed 3 and a catalyst bed 6 may be made to contain a water repellent agent if needed. Since the wastewater nature in a catalyst bed 3 can be raised and the depressor effect of flooding increases, especially the thing made to contain a water repellent agent in a catalyst bed 3 is desirable. However, since a water repellent agent is an insulator, the amount is so desirable that it is little, and the addition has desirable 0.01 - 15 mass %. As such a water repellent agent, meltable fluorine-containing resin etc. can be used for PTFE or a solvent.

[0051] Especially the formation approach of a cathode 5 and an anode 8 that consists of such a gaseous diffusion layer and a catalyst bed is not limited, and is manufactured according to the following formation approaches.

[0052] First, catalyst bed formation ink is prepared. Next, it sprays on the ingredient front face on which the layer which consists of polyelectrolyte film PEM, or a water repellent agent and carbon turns into gaseous diffusion layers, such as a carbon cross formed in the front face, and this catalyst bed formation ink is applied, and a filtration imprint is carried out, and the catalyst bed which has predetermined structure on the ingredient front face used as the polyelectrolyte film PEM or a gaseous diffusion layer is formed so that thickness may become homogeneity.

[0053] Next, junction into the ingredient used as the polyelectrolyte film PEM in which the catalyst bed was formed, and a gaseous diffusion layer, or junction into the ingredient used as the polyelectrolyte film PEM and the gaseous diffusion layer in which the catalyst bed was formed is performed. A hotpress and a roll press may perform above both junction. At this time, both may be joined by un-heating using special adhesives as indicated by JP,7-220741, A etc. Moreover, after forming a catalyst bed by spreading etc. on PTFE prepared beforehand, polyethylene terephthalate, etc. base material being monotonous, the so-called replica method which imprints this with a hotpress on the polyelectrolyte film PEM may be used. Thus, a cathode 5, an anode 8, and a unit cell UC are completed.

[0054] Here, when forming the catalyst bed 3 of the two-layer structure, you may carry out by carrying out direct two-times spreading of the catalyst bed formation ink for cathode formation for example, on the polyelectrolyte film PEM. In this case, the first spreading serves as a process which forms a catalyst bed 1, and spreading of a two-times eye serves as a process which forms a catalyst bed 2.

[0055] Furthermore, the desirable range changes with formation approaches of an electrode, and the thing of the viscosity range large from the thing of the shape of dispersion liquid which is dozens cP extent to the thing of the shape of a paste of 20,000cP extent can be used for the viscosity of the above-mentioned catalyst bed formation ink. In order to adjust viscosity, the thickener and the diluent solvent may be contained in catalyst bed formation ink.

[0056] As mentioned above, although the suitable operation gestalt of this invention was explained to the detail, this invention is not limited to the above-mentioned operation gestalt.

[0057] For example, in the above-mentioned operation gestalt, although the polymer electrolyte fuel cell equipped with the cathode which has the catalyst bed structure of a bilayer was explained, the polymer electrolyte fuel cell of this invention is not limited to this, and may be equipped with the cathode which has the catalyst bed structure of three or more layers.

[0058] In this case, it is desirable that the water content W of the ion exchange resin contained in two or more catalyst beds, respectively is missing from the outermost catalyst bed, and decreases from the

catalyst bed of the innermost section. Thus, the catalyst bed of the innermost section and the outermost catalyst bed can demonstrate effectively the role of efficient electrode reaction and the role of efficient wastewater which were meant by each by applying to the outermost catalyst bed from the catalyst bed of the innermost section, and establishing a negative inclination in the water content W of the ion exchange resin in each catalyst bed.

[0059] Moreover, it is desirable that the micropore rate in two or more catalyst beds of each is missing from the outermost catalyst bed, and decreases from the catalyst bed of the innermost section. Thus, applying a micropore rate to the outermost catalyst bed from the catalyst bed of the innermost section, and making it decrease turns into also making it increase from the catalyst bed of the innermost section to the outermost catalyst bed, applying the gaseous diffusion effective opening section. Therefore, it becomes possible by doing in this way to build still more certainly the catalyst bed which has the good wastewater structure where supply of the reactant gas and the proton which maintained the balance to the reaction site in each catalyst bed can be held over a long period of time.

[0060] Furthermore, in the above-mentioned operation gestalt, although the polymer electrolyte fuel cell which has the configuration of only a unit cell was explained, the polymer electrolyte fuel cell of this invention is not limited to this, and may have the so-called stack structure which carried out two or more laminatings of the unit cell.

[0061] Moreover, in the above-mentioned operation gestalt, although the so-called electrode and film zygote were explained as a unit cell, the polymer electrolyte fuel cell of this invention is not limited to this. For example, as an anode and a cathode are not joined to the polyelectrolyte film by heat treatment, respectively, an anode and a cathode are contacted on the polyelectrolyte film concerned to the polyelectrolyte film and each contact resistance of the anode and cathode to the polyelectrolyte film serves as the minimum value, you may make it pinch, where the polyelectrolyte film is dynamically pressurized from an outside with an anode and a cathode.

[0062] Furthermore, in the above-mentioned operation gestalt, although the polymer electrolyte fuel cell in the case of using the gas which uses hydrogen as a principal component as anode reaction gas was explained, the polymer electrolyte fuel cell of this invention may be the thing of a configuration of it not being limited to this and introducing methanol gas into an anode directly as anode reaction gas for example.

[0063]

[Example] Although an example and the example of a comparison are given and the contents of the polymer electrolyte fuel cell of this invention are explained in more detail hereafter, this invention is not limited to these examples. In addition, the water content W and IEC, the thickness, and the micropore rate of the ion exchange resin in which the description of the structure of the catalyst bed of each cathode is shown are shown in Table 1 about the polymer electrolyte fuel cell of the example shown below and the example of a comparison.

[0064] (Example 1) The unit cell of an example 1 was produced with the procedure explained below. The precursor of the ion exchange resin made to contain in a catalyst bed was first prepared in the following procedures. That is, diisopropyl peroxy carbonate and $\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}(\text{CF}_3)-\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ were taught to the autoclave made from stainless steel as a polymerization initiator. Next, after fully purging the gas in this autoclave by liquid nitrogen, tetrafluoroethylene was taught, the temperature in an autoclave was held at 40 degrees C, and bulk polymerization was started. In addition, the pressure in the autoclave under polymerization reaction was uniformly held by carrying out additional installation of the tetrafluoroethylene from the outside of a system. Next, the $\text{CF}_2=\text{CF}_2/\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}(\text{CF}_3)-\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ copolymer which is made to condense and wash and dry with a methanol the polymer solution which purged unreacted $\text{CF}_2=\text{CF}_2$ 10 hours after polymerization initiation, was made to end a polymerization, and was obtained, and turns into a precursor of ion exchange resin was obtained.

[0065] Next, made the precursor of the above-mentioned ion-exchange resin mix into the mixed water solution 15 mass % Containing dimethyl sulfoxide 30 mass % and KOH, it was made to hydrolyze, and the sulfonic acid type perfluorocarbon polymer was obtained by being immersed after rinsing and into the hydrochloric acid of one mol / L. Here, IEC compounded two kinds of ion exchange resin which is 1.1meq(s)/g and 0.9meq/g by adjusting the amount of a polymerization initiator, and the pressure at the time of a polymerization.

[0066] Next, the water content W of two kinds of compound ion exchange resin was measured in the following procedures. First, after dipping ion exchange resin into the 90-degree C warm water near cell operating temperature for 16 hours, and returning to a room temperature underwater further, surface

moisture was removed quickly and the swelling mass X_w of ion exchange resin was measured. Then, after carrying out reduced pressure drying of the ion-exchange resin into reduced pressure oven for 16 hours, using drying temperature as 120 degrees C, and returning this ion-exchange resin to the bottom of nitrogen-gas-atmosphere mind all over a dry box further even at a room temperature, that dry mass X_d was measured. And based on (4) types, it asked for the water content W of each ion exchange resin using this X_w and X_d .

[0067] Catalyst bed formation ink was prepared as follows. That is, a 40 mass % platinum support carbon particle and the liquid which distributed the mixed solvent (it is 1:1 at a mass ratio) of ethanol/water by [as setting IEC to 2:1 with a mass ratio in the ion exchange resin of 1.10meq(s)/g] were prepared as catalyst bed formation ink A. Moreover, the preparation conditions except having used the ion exchange resin which set IEC to 0.9meq(s)/g as catalyst bed formation ink B prepared the liquid made to be the same as that of catalyst bed formation ink A. Furthermore, the preparation conditions except having used the solvent as the mixed solvent (it being 4:1 at a mass ratio) of ethanol/water prepared the solution made to be the same as that of catalyst bed formation ink A as catalyst bed formation ink C.

[0068] The thing with a thickness of 350 micrometers to which the anode and the cathode carried out the weather strip of the water-repellent carbon cross (fiber textile fabrics) in the water-repellent carbon powder layer (mixture of carbon black and PTFE) was used for the gaseous diffusion layer of an electrode.

[0069] Furthermore, the cathode catalyst bed which has the two-layer structure was formed with the following procedures. That is, first, as a catalyst bed by the side of a gaseous diffusion layer, it applied once and the catalyst bed formation ink C for catalyst bed formation was dried so that the amount of platinum support might be on the water-repellent carbon powder layer side of the above-mentioned gaseous diffusion layer sheet with 0.3 mg/cm². Next, on it, as a catalyst bed by the side of the polyelectrolyte film, it applied once and catalyst bed formation ink A was dried so that the amount of platinum support might serve as 0.3 mg/cm². Thus, the cathode catalyst bed of the two-layer structure was formed. The amount of the platinum supported by the produced gas diffusion electrode for cathodes here was 0.6 mg/cm², and the thickness of a catalyst bed was 20 micrometers (the catalyst bed by the side of the polyelectrolyte film; 9 micrometers, catalyst bed; 11 micrometer by the side of a gaseous diffusion layer). In addition, the micropore rate of the catalyst bed by the side of the polyelectrolyte film was 93vol(s).%, and the micropore rate of the catalyst bed by the side of a gaseous diffusion layer was 78vol(s).%.

[0070] On the other hand, it applied and the catalyst bed of an anode dried the catalyst bed formation ink A for catalyst formation (IEC=1.10meq./g of resin) so that the amount of support of platinum might serve as 0.3 mg/cm² per time, and it was formed by repeating this process twice. The amount of the platinum supported by the produced gas diffusion electrode for anodes here was 0.6 mg/cm².

[0071] Moreover, the produced gas diffusion electrode cut down the anode and the cathode so that an effective electrode surface product might be set to 2.25cm. Furthermore, as polyelectrolyte film, the sulfonic acid type perfluorocarbon polymer (trade name: the deflection myon HR, the Asahi Glass [Co., Ltd.] Co., Ltd. make, IEC=1.1meq./g, 50 micrometers of desiccation thickness) was used.

[0072] It is the following, the polyelectrolyte film was made, it joined to the anode and cathode which were produced as mentioned above, and the so-called electrode and film zygote were produced. That is, the field where the cathode and the anode were applied to catalyst bed formation ink was made to turn and counter inside, and it was made to join by performing a hotpress, where the polyelectrolyte film is put between them.

[0073] (Example 2) As catalyst bed formation ink D, the 40 mass % platinum support carbon catalyst and the solution which distributed the mixed solvent (it is 1:1 at a mass ratio) of ethanol/water by [as setting IEC to 2:1:0.05 with a mass ratio in the ion exchange resin of 1.10meq(s)/g and the calcium carbonate as an ostomy agent] were prepared.

[0074] The electrode and the film zygote were obtained like the example 1 by performing washing processing by the acid and making an ostomy agent remove after spreading except having carried out the ostomy and having produced the catalyst bed by the side of a gaseous diffusion layer so that the amount of platinum support might become a gaseous diffusion layer sheet with 0.3 mg/cm² about this catalyst bed formation ink D.

[0075] (An example 3, an example 4, and the example 1 of a comparison - the example 5 of a comparison) The electrode and the film zygote were produced like the example 1 except having made it become IEC which shows the bilayer configuration of a cathode catalyst bed in Table 1, thickness, and a

micropore rate.

[0076] [Cell characteristic test] Each unit cell (an electrode and film zygote) of the above-mentioned example 1 - an example 4 and the example 1 of a comparison - the example 4 of a comparison was equipped with the separator, it considered as the measurement cel, and the current potential property of a measurement cel was measured using an electronic load and DC power supply (the Takasago factory company make, FK400L, and EW1750L). The Measuring condition was made into operating temperature;80 degree C of hydrogen inlet pressure;0.05MPa, air induction inlet pressure;0.05MPa, and a measurement cel, and measured aging over 1000 hours of the polarization property of the measurement cel in current density;1.0 A/cm². The test result of each of these unit cells is shown in Table 1.

[0077] In addition, in Table 1, the value of deltaW shows the difference (W1-W2) of the water content W1 of the ion exchange resin contained in the catalyst bed by the side of the polyelectrolyte film in the catalyst bed of a cathode which has the two-layer structure, and the water content W2 of the ion exchange resin contained in the catalyst bed by the side of a gaseous diffusion layer. Moreover, the value of deltaV shows the difference of the cell voltage (electrical potential difference between terminals) of the measurement cel in early stages of starting (after [of measurement initiation] about 250 minutes), and the cell voltage of each measurement cel after 1000-hour progress.

[Table 1]

| | カソード触媒層 | | | | | | | 電池特性 | | | |
|-------|---------------------------------|---|-----------------|----------------------------------|---|-----------------|------------|------------------|--|--|---|
| | 高分子電解質膜側の触媒層 | | | ガス拡散層側の触媒層 | | | ΔW | 開回路 電圧 /mV | 起動初期 の電池電圧 /mV at 1.0A·cm ⁻² | 1000h後 の電池電圧 /mV at 1.0A·cm ⁻² | 1000h後 の電池電圧 降下 ΔV /mV |
| | イオン 交換樹 脂の 含水率 W1/% | イオン 交換樹脂 のIEC /meq·g ⁻¹ | 微細孔割合 /vol.% | イオン 交換樹 脂の 含水率 W2 /% | イオン 交換樹脂 のIEC /meq·g ⁻¹ | 微細孔割合 /vol.% | | | | | |
| 実施例 1 | 30 | 1.10 | 93 | 20 | 0.90 | 78 | 10 | 950 | 590 | 580 | 10 |
| 実施例 2 | 30 | 1.10 | 92 | 20 | 0.90 | 68 | 10 | 940 | 580 | 570 | 10 |
| 実施例 3 | 45 | 1.30 | 94 | 32 | 1.15 | 82 | 13 | 950 | 630 | 570 | 60 |
| 実施例 4 | 21 | 0.95 | 90 | 15 | 0.80 | 77 | 6 | 940 | 570 | 570 | 0 |
| 比較例 1 | 30 | 1.10 | 93 | 30 | 1.10 | 89 | 0 | 950 | 600 | 540 | 60 |
| 比較例 2 | 20 | 0.90 | 90 | 20 | 0.90 | 87 | 0 | 940 | 550 | 540 | 10 |
| 比較例 3 | 30 | 1.10 | 93 | 26 | 0.97 | 85 | 4 | 950 | 590 | 540 | 50 |
| 比較例 4 | 81 | 1.15 | 89 | 32 | 1.15 | 80 | 49 | 960 | 620 | 480 | 140 |
| 比較例 5 | 18 | 0.80 | 89 | 15 | 0.80 | 80 | 3 | 940 | 530 | 530 | 0 |

[0078] In addition, it was checked that the cell voltage after operating the polymer electrolyte fuel cell of the example 3 of a comparison corresponding to the polymer electrolyte fuel cell of Japanese Patent Application No. 11-288727 to the cell voltage in early stages of starting for 1000 hours falls by no less than 50mV.

[0079]

[Effect of the Invention] As explained above, according to the polymer electrolyte fuel cell of this invention, it becomes possible to build the catalyst bed which has the good wastewater structure where supply of reactant gas to the secured reaction site can be held over a long period of time. Therefore, it becomes possible to prevent generating of the flooding in a cathode catalyst bed, and to use the reaction site in the catalyst bed concerned effectively especially, in the catalyst bed under actuation. Therefore, according to this invention, even if it is the case where make high the cell output in early stages of starting, and a high current is passed, generating of flooding is fully prevented, and the polymer electrolyte fuel cell which is stabilized and can obtain a high cell output from the early stages of starting over a long period of time can be offered.

[Translation done.]